

Trace metal analysis of atmospheric particulate matter: A comparison of personal and ambient samplers¹

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Abstract: This study compared the size-resolved trace metal concentrations from a standard ambient sampler to those of three commercial personal samplers. Trace metals data from each personal sampler were also inter-compared. Co-located “fixed site” samples were collected in two urban sites in the United States using three types of personal samplers (BGI PM2.5 cyclone, URG PM2.5 cyclone, and SioutasTM personal cascade impactor sampler [PCIS]) and one standard ambient sampler fitted with a PM2.5 cyclone. This experimental design enabled direct evaluation of the relative performance of the personal samplers. Results of mass measurements showed good agreement between the standard equipment and personal samplers; however, trace metal comparisons (measured by ICP-MS) showed reproducible concentration biases among personal samplers. These biases can be summarized as $BGI < URG < PCIS$ (0.27 ± 0.08 , 0.72 ± 0.08 , and 1.32 ± 0.34 relative to the ambient sampler). Elements exhibiting larger variation between personal samplers were associated with higher mass fractions in the coarse fraction, suggesting the PM2.5 size-cut a potential cause of this deviation.

Key words: size-cut, atmospheric aerosols, inductively coupled plasma – mass spectrometry (ICP-MS).

Résumé : Cette étude compare les concentrations de métaux traces obtenues par un échantillonneur standard de l'air ambiant à celles obtenues par trois échantillonneurs personnels disponibles sur le marché; les métaux traces sont classés selon leurs dimensions. Les données de métaux traces obtenues des échantillonneurs personnels disponibles sur le marché ont aussi été comparées entre elles. Les échantillons de « site fixe » cositués ont été collectés dans deux sites urbains aux États-Unis en utilisant trois types d'échantillonneurs personnels (BGI PM2,5 cyclone, URG PM2,5 cyclone et l'échantillonneur impacteur en cascade Sioutas^{MC} [PCIS]) ainsi qu'un échantillonneur standard d'air ambiant muni d'un cyclone PM2,5. Ce protocole expérimental permet l'évaluation directe du rendement relatif des échantillonneurs personnels. Les résultats des mesures des masses ont montré une bonne corrélation entre l'équipement standard et les échantillonneurs personnels; toutefois, les comparaisons des métaux traces (mesurés par ICP-MS) ont montré des biais de concentration reproductibles parmi les échantillonneurs personnels. Ces biais peuvent être résumés comme suit : $BGI < URG < PCIS$ ($0,27 \pm 0,08$, $0,72 \pm 0,08$ et $1,32 \pm 0,34$ relativement à l'échantillonneur d'air ambiant). Les éléments montrant une plus grande variation entre les échantillonneurs personnels ont été associés à la fraction plus grossière, suggérant que la dimension de coupure du PM2,5 soit une cause potentielle de cette déviation.

Mots-clés : dimension de coupure, aérosols atmosphériques, spectromètre de masse à plasma inductif (ICP-MS).

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Introduction

While trace metals are generally a minor component of atmospheric aerosols, health studies demonstrate the need to

properly characterize human exposure to these species. Many recent epidemiological studies have correlated an increase of atmospheric particulate matter (PM) with increases in deaths, asthma medication consumed, and hospitalization

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Table 1. Detection limits for ICP–MS analysis. Method detection limits are based on 24 h sampling periods at the airflow rates shown (in parentheses).

Metal	Detection limit (ng m ⁻³ air)			
	PCIS (9 L min ⁻¹)	AIHL (10.75 L min ⁻¹)	BGI (3.9 L min ⁻¹)	URG (3 L min ⁻¹)
Iron	0.65	0.54	1.67	1.94
Barium	0.97	0.81	2.50	2.92
Copper	0.97	0.81	2.50	2.92
Manganese	1.46	1.22	3.75	4.38
Lead	0.16	0.14	0.42	0.49
Vanadium	1.30	1.09	3.33	3.89

for respiratory problems in children (Clancy et al. 2002; Mortimer et al. 2002; von Klot et al. 2002; Ghio et al. 2003; Peden 2005; Pope and Dockery 2006). There is also strong evidence suggesting that persistent exposure to various trace metals can result in adverse health effects. For example, several studies have linked the inhalation of transition metals to inflammation of lung tissue and to an increase of reactive oxygen species in the lungs (Johansson et al. 1992; Ghio and Devlin 2001; Sun et al. 2001; Pagan et al. 2003). In another study, a drastic decrease in hospital visits was observed for children with pneumonia, bronchitis, and asthma following the closure of a local steel mill (Pope 1989).

To better quantify and characterize a person's actual exposure to PM, it is becoming increasingly common for researchers to employ personal samplers (Hopke et al. 2003; Yip et al. 2004). Personal samplers allow for a more direct measurement of personal exposure to trace metals. Validation of these samplers is typically performed in two stages. First, the individual size-cuts are measured by generating spherical aerosols of a known diameter and the collection efficiency of relevant sizes are tested (Misra et al. 2002; Hering et al. 2003).

Further validation is accomplished by performing field studies of the sampler against well-characterized samplers. Historically, personal samplers have been validated using measures of mass concentration, major ion concentration (e.g., nitrate and sulfate), and (or) elemental and organic carbon (EC and OC) comparisons (Singh et al. 2003). To validate the ADI (Hering et al. 2003) sampler, mass, nitrate, sulfate, EC, and OC concentrations were compared to one other sampler (AIHL). For both coarse and fine particulate mass, The Sioutas personal cascade impactor sampler (PCIS) was compared to another size-resolved sampler, the micro-orifice uniform deposit impactor (MOUDI), an APS and a SMPS. Size-resolved nitrate, sulfate, and EC were also compared against the MOUDI. Validation of personal samplers for assessing trace metal exposure has not been performed, yet they have been assumed by some research groups to be adequate for trace metal sampling (Graney et al. 2004; Chillrud et al. 2005).

The small filter loadings, coupled with relatively low concentrations of metals in ambient atmospheric particles, required the development and use of ultra-trace chemistry optimized methods. A low volume aerosol digestion method was developed in this study to minimize analytical blanks and maximize signal and noise. This digestion method was coupled with high sensitivity inductively coupled plasma – mass spectrometry (ICP–MS) techniques to provide detec-

tion limits below 1 ng m⁻³ air for a majority of metals. The relevant detection limits for this technique are listed in Table 1 for the various samplers tested in this study. Individual metal concentrations for PM samples were found to range from 6 to 600 ng m⁻³ air.

The metals examined in the intercomparison are iron, manganese, barium, copper, lead, and vanadium and were chosen based on one or both of the following criteria: (1) their unique source apportionment characteristics and (2) their importance to human and environmental health. Iron in particulate phases with an aerodynamic diameter >2.5 µm has primary sources from both resuspended crustal material and automobile brake-wear. Barium is also a common element found in automobile brake-wear (Garg et al. 2000). The primary source of iron found in PM_{2.5} aerosols has been reported to be from the combustion of coal and from steel mills (Suarez and Ondov 2002). However, in regions such as the Los Angeles Basin, automobile sources are an important source of fine particulate iron (Singh et al. 2002). Vanadium is used as a tracer for fuel oil combustion (Divita et al. 1996). Manganese and lead were chosen as representative air toxins — both are known neurotoxins. Iron, vanadium, copper, and barium are known to cause inflammation in lung tissue (Camner and Johansson 1992; Carter et al. 1997).

Due to the relatively low mass loadings often observed on filters collected from personal samplers, analysis of trace metals in these samples poses a significant challenge. Not only must analysts consider the problem of low signal, but the magnitude of the bias between different samplers is currently unknown. As more researchers utilize personal samplers in their studies, there is a growing need to quantify the extent of variation (if any) between these samplers. In this intercomparison study, we evaluated three personal samplers for the measurement of trace metals in two sampling sites. Further, a low-volume microwave-assisted digestion procedure for the solubilization of metals in atmospheric particles was used to improve signal and noise. The primary goal of this study is to determine, using “real-world samples,” whether any biases between personal samplers are apparent.

Methods

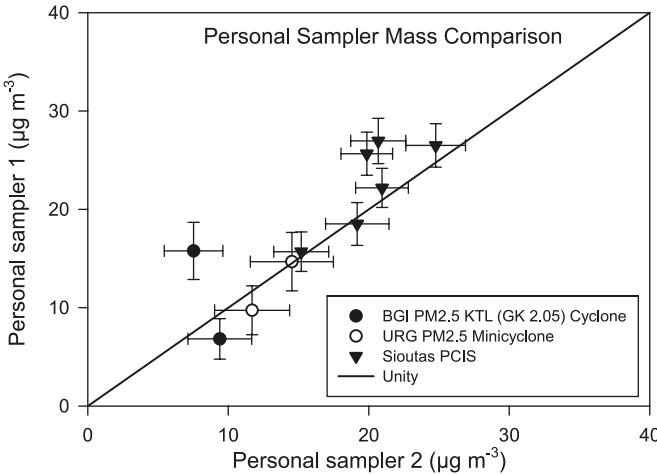
The current study compared concentrations of trace metals measured in ambient particulate matter samples collected at two locations from four co-located samplers: one standard stationary atmospheric sampler that employs an Air and Industrial Hygiene Laboratory (AIHL) cyclone with two

Table 2. Sampling protocol for the East St. Louis, Ill. and the Los Angeles, Calif. sites.

Protocol	Total number of sampling days ^a	
	Los Angeles	East St. Louis
AIHL Cyclone	5	2
URG-2000-30EQ	5	2 ^a
PCIS	5 ^a	2 ^a
BGI PM2.5 KTL (GK 2.05)	5	2 ^a

^aIndicates that duplicate samplers were deployed at this site.

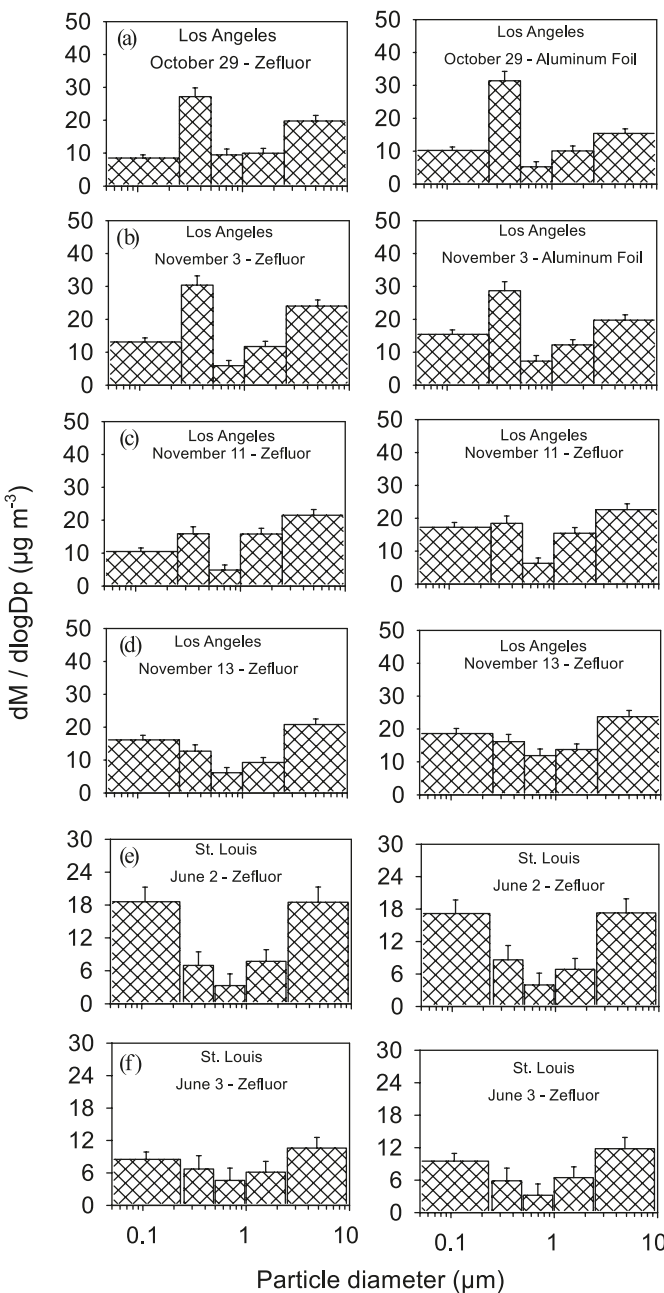
Fig. 1. Comparison of PM2.5 mass from co-located personal samplers from Los Angeles and East St. Louis, Ill.



PM2.5 filter holders (John and Reischl 1980), and three different personal samplers including one BGI PM2.5 KTL (GK 2.05) cyclone, one URG PM2.5 minicyclone (URG-2000-30EQ), and two Sioutas™ personal cascade impactor samplers (PCIS) (Misra et al. 2002; Singh et al. 2003). The PCIS sampler collects particles in five different aerodynamic size ranges: > 2.5 µm, 2.5–1 µm, 1–0.5 µm, 0.5–0.25 µm, and <0.25 µm. For all PM2.5 data reported here from the PCIS, the bottom four stages were analyzed independently, and summed. The overall analytical uncertainties for the PM2.5 measurements have also been summed across the four stages. The PM2.5 samplers that use the AIHL cyclone (often referred to as the RAAS2.5-300, used in the Andersen sampler) have been certified for the Environmental Protection Agency (EPA) speciated trends network (STN) and many researchers have used this cyclone (Nolte et al. 2001; Peters et al. 2001; Solomon et al. 2001; Dillner et al. 2006).

The sampling site in Los Angeles was at the main campus of the University of Southern California near downtown Los Angeles. This sampling location is about 150 m downwind of a major freeway and represents an urban mix of industrial, vehicular, and construction aerosol sources. All samplers used in this study were operated under the manufacturer’s recommendations. One ambient AIHL PM2.5 cyclone (John and Reischl 1980) was operated at 21.5 L/min where the flow was equally split for two collection substrates (47 mm Teflon filters, Teflo, 2.0 µm pore size, Pall Life Sciences Inc). This sampler was co-located with four personal samplers: (1) two Sioutas™ cascade im-

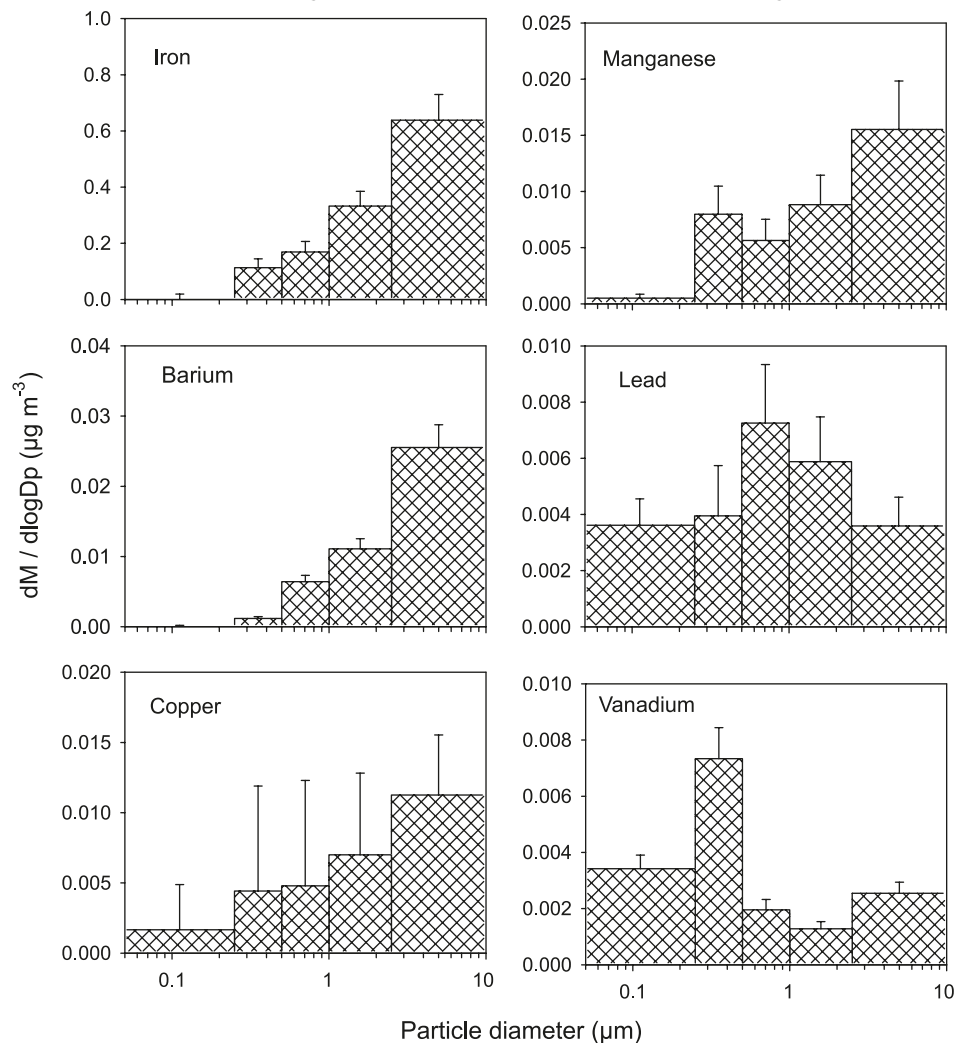
Fig. 2. Total size-resolved mass concentrations collected from the PCIS.



pactor samplers (PCIS) with five size-resolved stages operated at 9 L/min with 25 mm impactor substrates (Zefluor, 3.0 µm or high purity aluminum foils) for all stages except a 37 mm substrate as an after-filter (Teflo, 2.0 µm pore size, Pall Life Sciences Inc), (2) One BGI PM2.5 KTL (GK 2.05) cyclone operated at 3.9 L/min using 37 mm substrates (Teflo, 2.0 µm), and (3) One URG PM2.5 minicyclone (URG-2000-30EQ) operating at 3.0 L/min was used with 25 mm substrates (Teflo, 2.0 µm). Samples were collected for 24 h periods over the course of five sampling days.

Sampling in East St. Louis, Ill, USA took place at the EPA-funded Midwest Supersite. The East St. Louis site is in an urban residential – light commercial area and is about 3 km east of St. Louis, Mo. The sampling design at this site

Fig. 3. Size-resolved trace metals data from Los Angeles, Calif. collected on 29 October 2003 using the PCIS on Zefluor substrates.



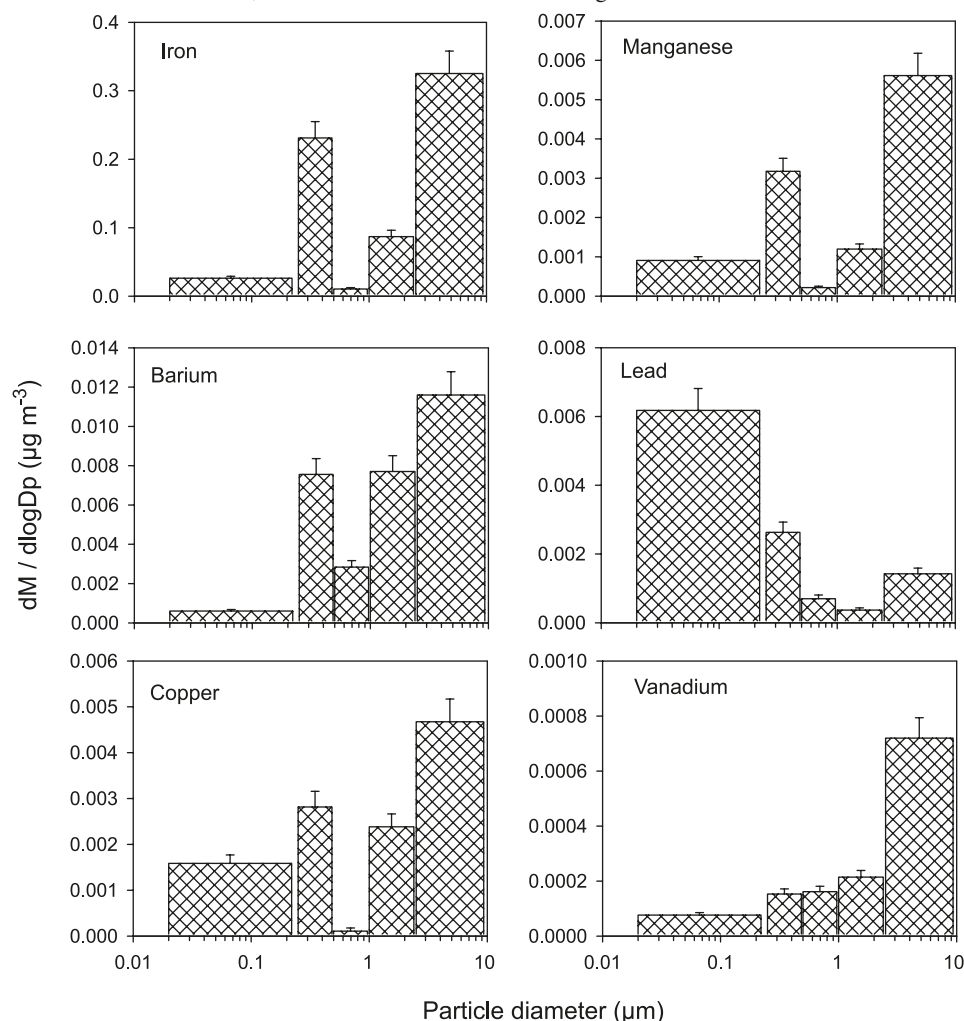
focused not only on the comparison of personal samplers to an ambient sampler, as was the focus in Los Angeles, but also compares trace metals data between co-located duplicate personal samplers. Therefore, the same set of samplers was used as at the Los Angeles site, however duplicate samples were also obtained. Samples were collected for 24 h periods over the course of two sampling days. A summary of the sampling protocol can be seen in Table 2. Table 2 shows that duplicate samples were collected for all personal samplers in East St. Louis while duplicate samples were only collected using the PCIS sampler in Los Angeles. At both sites, a rotometer was used to measure the flow rates of each sampler before and after sampling. The reported flow rates are the average of these two values. Sampling days with air flow deviations >10% of the manufacturer's recommended flow rate were discarded and are not included in this study.

Total particulate matter elemental concentration measurements were achieved using a method that coupled low-volume microwave-assisted acid digestion with inductively coupled plasma – mass spectrometry (ICP-MS). The polymethylpentane support ring from the Teflo filter is removed and the filter membrane is placed in a Teflon digestion

bomb with a mixture of high purity acids (1.0 mL 16 N HNO₃, 0.25 mL 12 N HCl, 0.1 mL 28 N HF). The PM samples were digested by subjecting the sealed Teflon bombs to a programmed microwave digestion (Ethos, Milestone) [9 min temperature ramp to 180 °C followed by a 10 min hold at 180 °C] and diluted to 15 mL with > 18.0 MΩ water. A typical analytical batch consisted of 22 unknowns, 6 standard reference materials (SRMs), 4 matrix blanks, 2 method blanks, and 2 matrix spikes. These included the NIST SRMs: recycled auto catalyst (#2556), urban dust (#1649a), and San Joaquin soil (#2709).

Trace metal clean techniques were used throughout all phases of sampling and analysis. All pre- and post-sampling handling of the substrates were performed in a dedicated trace metal clean room. Before use, all collection substrates were subjected to rigorous washing protocols, which have been shown to minimize trace metal contamination (Schauer et al. 2006). For Teflon materials, this procedure includes a series of three rinses: trace metal grade hydrochloric acid (Fisher), trace metal grade nitric acid (Fisher), followed by >18.0 MΩ water. Prior to sampling, the aluminum substrates were rinsed and sonicated in dichloromethane followed by methanol. All substrates were conditioned in a

Fig. 4. Size-resolved data from East St. Louis, Ill. collected on 2 June 2006 using the PCIS on Zefluor substrates.



constant temperature and relative humidity environment for at least 24 h and weighed, in triplicate (Mettler Toledo-MX5 Microbalance), pre- and post-sampling. The reported sensitivity of this balance is $\pm 0.8 \mu\text{g}$.

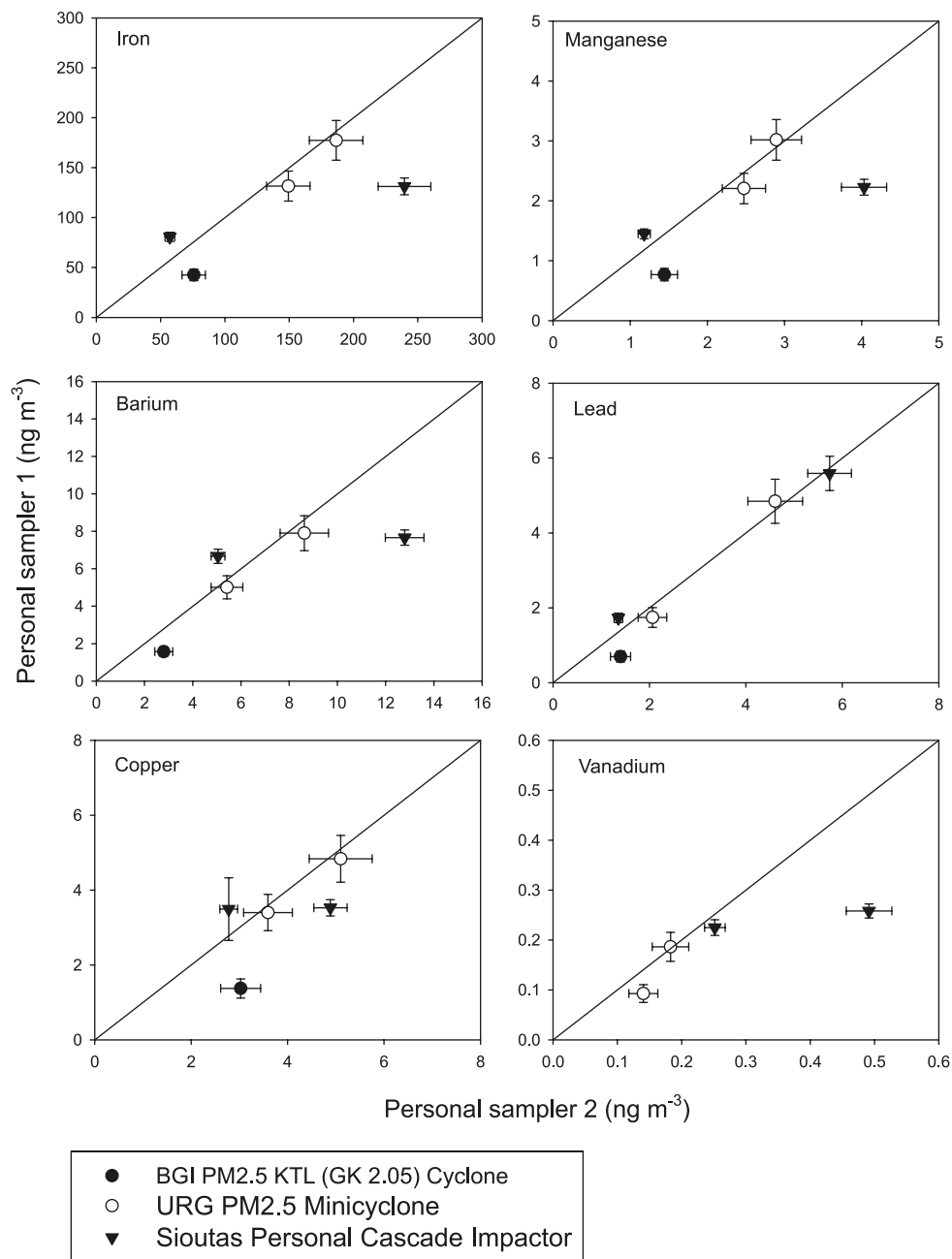
Results and discussion

Figure 1 presents a comparison of $\text{PM}_{2.5}$ mass concentration ($\mu\text{g m}^{-3}$) collected from duplicate samplers at each sampling site. The samplers in this Figure include the BGI $\text{PM}_{2.5}$ KTL (GK2.05) (2 d in East St. Louis), URG $\text{PM}_{2.5}$ Minicyclone (2 d in East St. Louis), and the SioutasTM PCIS (4 d from Los Angeles and 2 days from East St. Louis) duplicate samplers. Mass loadings of each size fraction of the PCIS ranged from 15 to 200 μg while typical loadings for the BGI and URG samplers were generally around 100 μg ranging from 35 to 160 μg per filter. The graph in Fig. 1 shows good agreement between co-located personal samplers, as most are within 10% of the 1:1 line. The most significant outlier is a filter collected using the BGI sampler and was collected on 2 June 2006. Upon visual inspection of the two filters collected from the BGI sampler on this day and comparison of the filter masses with the co-located ambient $\text{PM}_{2.5}$ sample, it became apparent that one of the

BGI samplers was not functioning properly and was therefore not used for any of the subsequent metal comparisons. The size-resolved total PM mass concentrations of the co-located PCIS samplers are plotted in Fig. 2. This plot generally shows excellent agreement between PCIS samplers for each size fraction. The 6 November 2003 PCIS size distribution is not shown here as no co-located PCIS sampler was used on this day.

Figure 3 presents PCIS size distributions for the Los Angeles site of six different metals for 29 October 2003. These plots are representative of the elemental distributions measured at this site during this sampling campaign. In Los Angeles, with the exception of lead and vanadium, the coarse fraction (size of 2.5 μm or greater) is enriched in trace metals in comparison with $\text{PM}_{2.5}$ size fractions. Vanadium exhibits the largest relative contribution in the fine and ultra-fine modes. The size distribution of lead revealed a mode at approximately 0.5 μm , that is consistent with past studies (Allen et al. 2001). As expected, iron levels (Fig. 3) far exceed those of the other metals (50–100 times greater) and its size distribution is dominated by the coarse fraction of particles in Los Angeles. A large fraction of barium is also present in the coarse fraction. Manganese displays a bimodal

Fig. 5. Comparison of PM_{2.5} metals air concentration from co-located personal samplers from East St. Louis, Ill. The error bars represent the analytical uncertainty as well as the uncertainty with respect to sampling.

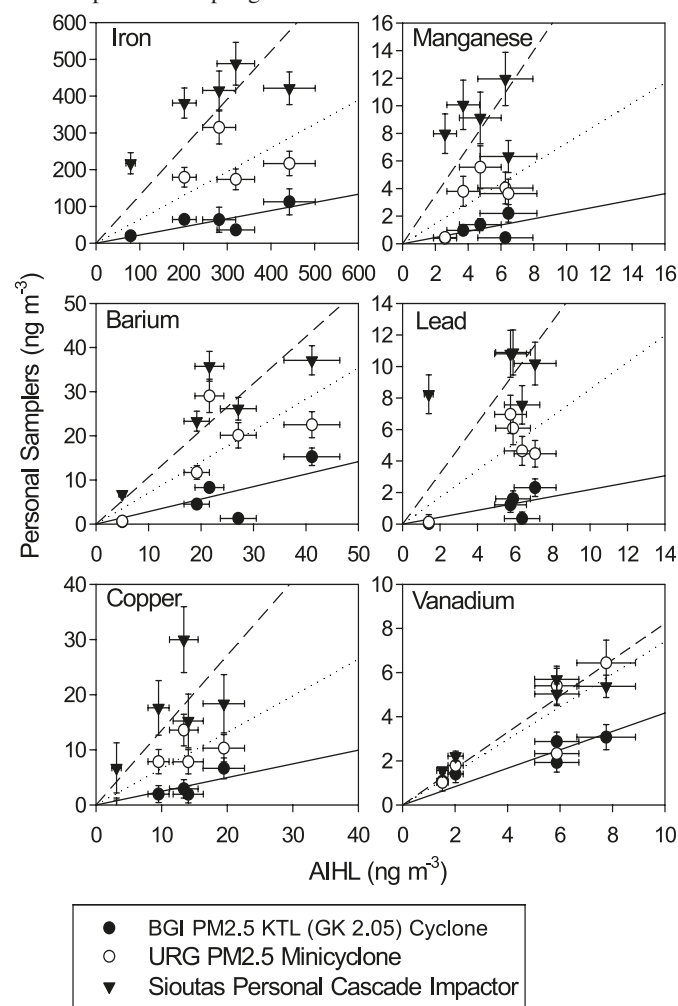


distribution, with one very small mode at around 1–0.5 μm and then one mode in the $>2.5 \mu\text{m}$ range. This is in agreement with other studies (Allen et al. 2001) and likely indicates multiple sources.

Size-distribution plots paralleling those from Los Angeles are shown in Fig. 4 for the East St. Louis site on 2 June 2006. In general, the air concentrations of these six metals are approximately 2 times lower than those in Los Angeles. A more important difference is noted in the size-distributions, however. In Los Angeles, the elements iron, manganese, barium, and copper showed a consistent decreasing

trend as particle size decreased. In East St. Louis, bimodal distributions are observed: a large coarse component is present, but they also all show a significant mode in the 0.5–0.25 μm fraction, which is absent in the Los Angeles samples. The lead size distribution in East St. Louis has a very large ultra-fine component with a very small relative coarse component, whereas the Los Angeles site showed a relatively even size distribution with significant coarse and fine fractions. The vanadium size distributions between the sites are also radically different. In East St. Louis, the vanadium is concentrated in the coarse fraction whereas in Los

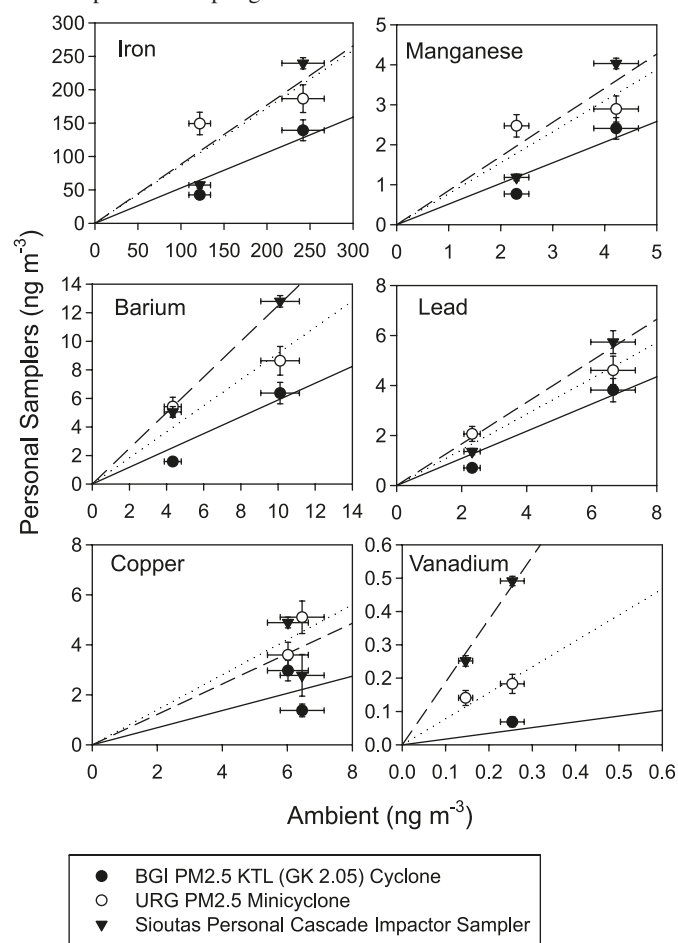
Fig. 6. PM_{2.5} Trace metal comparison of personal samplers versus the AIHL ambient sampler in Los Angeles, Calif. Note that the y-intercepts have been forced through zero and the error bars represent the analytical uncertainty as well as the uncertainty with respect to sampling.



Angeles, the vanadium is concentrated in the PM_{1.0} fraction.

A direct comparison of metal concentrations from co-located personal samples collected in East St. Louis is presented in Fig. 5. It should be noted this data is only for a sample set of two sampling events, and is not necessarily representative of these samplers under all conditions. The aforementioned BGI sample is not included due to disagreement in total PM_{2.5} mass (see Fig. 1). The error bars in these plots represent the analytical uncertainty of the ICP-MS measurement as well as the uncertainty associated with the subtraction of the loading blanks. It is clearly seen that the URG PM_{2.5} minicyclone is the most reproducible sampler for the metals presented here. This may be due to sampler design or operations, but it should be noted that these samples were collected under real-world conditions. The PCIS samples collected on 3 June 2006 also generally show very good agreement. However, significant differences are present for the co-located PCIS samplers on the 2 June 2006 sampling day. This is especially evident in iron, manganese, barium, copper, and vanadium. Upon further inspection

Fig. 7. PM_{2.5} Trace metal comparison of personal samplers versus the PM_{2.5} ambient sampler in East St. Louis, Ill. Note that the y-intercepts have been forced through zero and the error bars represent the analytical uncertainty as well as the uncertainty with respect to sampling.



tion of the metal content in individual size-fractions, it was found that only one size fraction (2.5–1 μm) consistently accounts for this deviation. The other four size fractions show very good agreement in terms of metals concentration (data not shown). The co-located BGI samplers consistently show different metal contents with one sampler always greater than the other.

Air concentrations of the metals from the personal samples collected in Los Angeles (PM_{2.5} only, summed concentrations of individual stages for the PCIS) are compared to the AIHL sampler for each metal in Fig. 6 (note that the y-intercepts have been forced through zero). A very clear trend is seen in the PM_{2.5} concentrations for all of the metals except for vanadium where the co-located PCIS > AIHL > URG > BGI (vanadium concentrations from the AIHL are greater than the PCIS). Also evident is a wide and consistent distribution pattern between personal samplers for all metals shown except for vanadium. In the case of vanadium, the slopes of the URG and the PCIS samplers are not different using a 95% confidence interval, nor is the slope of the BGI sampler different from the PCIS curve using a 95% confidence interval. However, for all other metals measured in Los Angeles, the slopes of the regressions com-

Table 3. PM_{2.5} mass and trace metal comparisons from Los Angeles by two different methods: (1) average of the individual personal sampler/ambient values and (2) regression slopes from the plots of the personal sampler vs. the ambient (Fig. 6). The uncertainties represent ± 1 standard deviation from the average.

	Average ratio (personal sampler/ambient)			Regression slopes (personal sampler vs. ambient)		
	BGI	URG	PCIS	BGI	URG	PCIS
PM _{2.5} mass	0.84 \pm 0.22	1.03 \pm 0.15	1.03 \pm 0.20	0.81	0.99	0.99
Iron	0.23 \pm 0.08	0.61 \pm 0.43	1.7 \pm 0.7	0.22	0.64	1.30
Manganese	0.22 \pm 0.11	0.71 \pm 0.40	2.1 \pm 0.8	0.23	0.73	1.75
Barium	0.23 \pm 0.15	0.68 \pm 0.44	1.2 \pm 0.3	0.28	0.71	1.06
Lead	0.18 \pm 0.13	0.74 \pm 0.43	2.5 \pm 1.9	0.22	0.86	1.61
Copper	0.18 \pm 0.12	0.58 \pm 0.38	1.7 \pm 0.60	0.25	0.66	1.36
Vanadium	0.52 \pm 0.17	0.74 \pm 0.21	0.93 \pm 0.16	0.42	0.74	0.82

Table 4. PM_{2.5} mass and trace metal comparisons from St. Louis by two different methods: (1) average of the individual personal sampler/ambient values and (2) regression slopes from the plots of the personal sampler vs. the ambient (Fig. 7). The uncertainties represent ± 1 standard deviation from the average.

	Average ratio (personal sampler/ambient)			Regression slopes (personal sampler vs. ambient)		
	BGI	URG	PCIS	BGI	URG	PCIS
PM _{2.5} mass	0.68 \pm 0.27	0.99 \pm 0.03	1.35 \pm 0.05	0.77	1.00	1.17
Iron	0.46 \pm 0.16	1.00 \pm 0.32	0.73 \pm 0.37	0.53	0.86	0.88
Manganese	0.45 \pm 0.17	0.88 \pm 0.27	0.73 \pm 0.31	0.52	0.77	0.85
Barium	0.50 \pm 0.19	1.05 \pm 0.28	1.22 \pm 0.07	0.59	0.92	1.25
Lead	0.44 \pm 0.19	0.79 \pm 0.14	0.72 \pm 0.20	0.54	0.71	0.83
Copper	0.35 \pm 0.20	0.69 \pm 0.14	0.62 \pm 0.27	0.34	0.70	0.61
Vanadium	0.14 \pm 0.19	0.84 \pm 0.17	1.83 \pm 0.15	0.17	0.78	1.88

paring the personal samplers with the AIHL sampler are statistically different (using a 95% confidence interval). Figure 7 (again, note that the intercepts have been forced through zero) shows similar plots for the two sampling days at East St. Louis. The East St. Louis personal samplers show a similar trend in PM_{2.5} metal concentrations to that measured in Los Angeles, with PCIS > URG > BGI. In contrast with the trend observed in Los Angeles, vanadium shows the only significant variance (using a 95% confidence interval) between personal samplers among the metals shown. The slopes between personal samplers for all of the other metals (Fe, Mn, Ba, Pb, Cu) are similar (95% confidence interval) at the East St. Louis site.

Personal samplers show a higher degree of variability for some metals than others and the variability changes depending on the sampling site. To help determine the cause of this observation, the size-distributions shown in Figs. 3 and 4 for each metal at each sampling site need to be examined. As mentioned earlier, all metals except for vanadium had a higher mass fraction in the coarse PM mode fraction in Los Angeles compared to the East St. Louis site. With this in mind, one can compare the plots in Figs. 6 and 7 and note that, when a higher fraction of the metal is in the fine and ultra-fine fractions, the personal samplers are closer in agreement. This is most clearly evident in the case of vana-

dium, which in Los Angeles is primarily found in the fine fraction (Fig. 3) and the personal samplers show a much closer relationship (Fig. 6) than in East St. Louis, where the vanadium is primarily in the coarse fraction (Fig. 4) and the personal samples are widely different (Fig. 7). In fact, when applying this method to all of the metals, we observe a better agreement across personal samplers when a higher fraction of the metal is present in the fine and ultra-fine fractions relative to the coarse fraction.

To quantify the average differences between personal samplers relative to the ambient sampler, the average slopes in Figs. 6 and 7 are presented in Table 3 and Table 4, respectively. The slopes for each sampler in Los Angeles, when averaging across all of the metals are 0.27 ± 0.08 , 0.72 ± 0.08 , and 1.32 ± 0.34 for the BGI, URG, and PCIS sampler, respectively. In East St. Louis, the regression slopes averaged across all metals are 0.45 ± 0.16 , 0.79 ± 0.09 , and 1.05 ± 0.46 for the BGI, URG, and PCIS sampler, respectively. The uncertainty represents one standard deviation of all metals. Details for each metal can be seen in Table 3 and Table 4 for the Los Angeles and East St. Louis samples, respectively. For comparison, the arithmetic mean of the metal concentration for the personal sampler compared to the ambient sampler for each metal is also shown in Table 3 and Table 4 for each site. This comparison shows

that the arithmetic means compare well to the slopes from the regression.

Conclusions and summary

In this study, atmospheric particulate matter (PM) was collected to assess the relative performance of three personal samplers and to compare them with fixed ambient monitors. Our results indicate that the total PM_{2.5} mass concentration derived from the personal samplers agreed reasonably well with each other and with the ambient sampler, implying that the overall performance of the personal samplers for this metric was satisfactory.

Using the SioutasTM personal cascade impactor sampler (PCIS), we were able to analyze atmospheric particles for size-resolved trace metals. The results presented in this study show that, in the Los Angeles area, a large contribution of trace metal mass is concentrated in the coarse fraction (>2.5 µm) of atmospheric particles. As fine particles are most likely to penetrate deep into the lungs, most health studies focus on this fraction. However, the soluble metals present in the coarse fraction of aerosols can also be a health concern. As many researchers point out, the soluble fraction of metal is often the most dangerous to human health (Carter et al. 1997; Adamson et al. 1999). Since there may be a large contribution of trace metals in the coarse fraction, collecting particles of only 2.5 µm or less may significantly underestimate the implications of atmospheric trace metals on human health.

Inter-sampler comparisons revealed large differences in aerosol trace metal concentrations, as clearly indicated by the data plotted in Figs. 6 and 7, with the variance between personal samplers dependent on the size distribution of the metal. This dependence on size-fraction is likely due to the inherent differences in PM_{2.5} size-cuts between personal samplers. When measuring the bulk species of aerosols (i.e., mass, elemental carbon, organic carbon), these differences are not as noticeable, as small changes are generally well within the analytical uncertainties. However, due to the trace concentrations of most metals, small differences in sampler size-cuts will likely make a large relative difference in concentrations, as is shown here for iron, manganese, barium, copper, lead, and vanadium. While there is no method of measuring the true air concentration of trace metals, it is apparent that comparing atmospheric particulate trace metal concentrations from different personal samplers could lead to erroneous conclusions and relative comparisons should be made only between the same types of personal sampler.

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